Russian Chemical Reviews **67** (5) 423 – 433 (1998) © 1998 Russian Academy of Sciences and Turpion Ltd

UDC 547.313

Reactions of thiocyanogen and thiocyanogen halides with unsaturated compounds

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Abstract. Data on the reactions of thiocyanogen and thiocyanogen halides with unsaturated compounds are systematised. The kinetic, stereo-, and regiochemical regularities of these reactions are analysed. The bibliography includes 81 references.

I. Introduction

Reactions of thiocyanogen and thiocyanogen halides with alkenes belong to the important methods used for the preparation of organic isothiocyanates and thiocyanates. The presence of several reaction centres in these compounds[1,2] opens up wide prospects for their application in the synthesis of diverse heterocyclic compounds.[3–14] Organic isothio- and thiocyanates and compounds based on them possess fungicidal and bactericidal activity,[15–17] manifest properties of optically active crystals[18] and organic superconductors.[19]

The ability of thiocyanogen to add to a double bond served as a basis for the development of a method for the quantitative determination of the degree of unsaturation of individual organic compounds, fats, and oil[20] (the thiocyanogen value).

Despite the practical importance of alkene thiocyanation, its mechanism remained poorly studied for a long time. It was stated that the chemical properties of thiocyanogen, $(SCN)_2$, and thiocyanogen halides are similar to those of halogens; in view of this, they are often called pseudo-halogens.[21] In the middle of the 1960s, the first studies on the stereochemistry and mechanism of reactions of thiocyanogen and thiocyanogen halides with alkenes appeared. To date, a large body of experimental data have been obtained; they require systematisation and reviewing.

We have made an attempt to generalise the data available on the reactions of thiocyanogen and thiocyanogen halides with unsaturated compounds both under conditions of electrophilic addition and under UV irradiation.

II. Reactions of thiocyanogen and thiocyanogen halides with alkenes under heterolytic conditions

Thiocyanogen was first isolated in an analytically pure form in 1919.[22] It is a very unstable compound with m.p. -2 °C, but its solutions in organic solvents are stable for rather long periods of time.[22–24]

IR Spectra of thiocyanogen in carbon disulfide and pentachloroethane[25] are in favour of its disulfide structure (structure **1**)

N≡C—S—S—C≡N,
1

However, the main absorption band in the IR spectra recorded in ether is somewhat shifted towards lower frequencies, whence a conclusion was made[25] that the isothiocyanate form (structure **2**) of thiocyanogen in ether is preferred

S=C=N—N=C=S.
2

This assignment is doubtful. For example, a similar shift of the absorption band in the IR spectra of thiocyanogen iodide was explained[26] by the formation of a charge-transfer complex of thiocyanogen iodide with ether as a low-basic solvent.

The coincidence of the heat of formation of thiocyanogen found experimentally with the theoretical value calculated assuming the disulfide structure[27–29] is in favour of structure **1**. It was confirmed by UV spectroscopic data for thiocyanogen in the gas phase and by theoretical calculations.[30]

Thiocyanogen chloride can be obtained quantitatively by the reaction of chlorine with $(SCN)_2$[25] or with AgSCN[31] in the gas phase or in organic solvents. However, it decomposes rapidly in solutions.[25,32] Mass spectrometric studies showed that the potential for formation of the SCN^+ particle from thiocyanogen chloride is lower than the potential for its formation from $(SCN)_2$.[29]

According to the data of IR,[25,33] microwave,[34] and photoelectron spectroscopy,[35] structure **3** is preferable for thiocyanogen chloride to structure **4**.

Cl—S—C≡N **3** Cl—N=C=S **4**

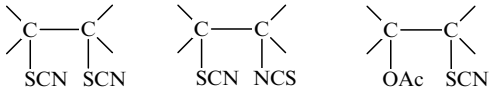
The data available to date indicate that the S–Cl bond in the thiocyanogen chloride molecule is polarised under heterolytic reaction conditions.

1. Main pathways of the reaction of thiocyanogen and thiocyanogen chloride with alkenes

Benzene, chloroform, and other non-nucleophilic solvents, as well as acetic acid, are the most common solvents used in reactions of alkenes with thiocyanogen. As a rule, these reactions result in a mixture of adducts, *i.e.*, dithiocyanates **5** and isothiocyanatothiocyanates **6**; in solutions in acetic acid, solvato-adducts **7** are also formed.

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Received 1 July 1997
Uspekhi Khimii **67** (5) 474–485 (1998); translated by S S Veselyi

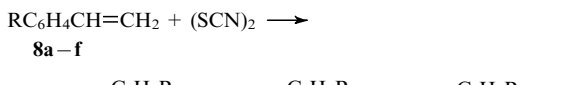


5 **6** **7**

It was shown[36,37] that the reaction rate increases with an increase in the solvent polarity and in the electron-donating properties of the substituent at the double bond of the alkene.

It was found in a study of the reaction of styrenes with thiocyanogen in AcOH that the second-order reaction constants correlate with the Brown–Okamoto constants (σ^+) of substituents. The reaction constant ρ^+ is -5.3.[38] These data indicate the electrophilic character of the reaction and a considerable polarity of the transition state.[38]

The products of the reaction of styrenes **8a–f** with thiocyanogen in acetic acid include 1-(aryl)ethane-1,2-diyldithiocyanates **9a–f**, 2-(aryl)-2-isothiocyanatoethyl thiocyanates **10a–f**, and products of the conjugate addition of acetic acid, *i.e.* 2-(aryl)-2-acetoxyethyl thiocyanates **11a–f**. The yields of the latter depend on the electron-donating properties of the aryl substituent (Table 1).[38,39] Thus, the introduction of electron-withdrawing substituents into the benzene ring of styrene increases the yields of thiocyanates **11a–f**, whereas electron-donating substituents decrease the yields.



The adducts **10** and solvato-adducts **11** are formed regioselectively. Similar regiochemistry of the formation of compounds **10** is observed in the reaction of $(SCN)_2$ with styrene **8c** in benzene (Table 1).[40]

The high polarity of the transition state (the limiting step of the reaction of thiocyanogen with alkenes) is evident from the greater effect of $LiClO_4$ on the overall reaction rate in comparison with the effect of this salt on the sulfenylhalogenation of alkenes.[39] In reactions with styrene[39] and cyclohexene,[41] the second-order reaction constants depend linearly on the $LiClO_4$ concentration according to Eqn (1)

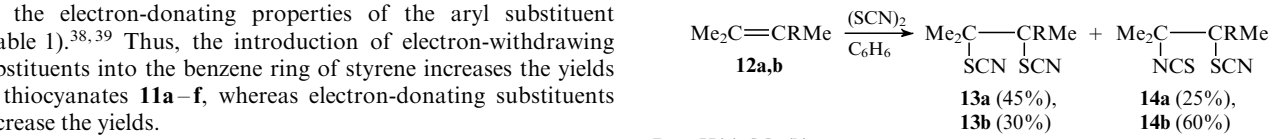
$$k_{exp} = k_0(1 + b[LiClO_4]), \quad (1)$$

where k_{exp} and k_0 are the observed reaction rate constants in the presence and in the absence of the salt, respectively. The b parameter varies from 17 to 38 depending on the reaction temperature and the alkene structure,[39] whereas for sulfenylhalogenation, it varies from 4.5 to 8.[39,42–44]

The formation of adducts **6** with isothiocyanate groups is undoubtedly related to the ambidentate properties of the thiocyanate anion. The table below lists the charge distributions in the SCN^- anion calculated by MO LCBO (method A)[45] and by MO LCAO in the Wolfberg–Helmholtz (method B)[46] and Hückel approximations (method C).[47]

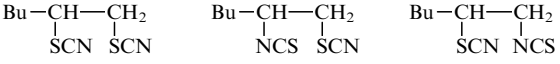
Method	Charge distribution on atoms		
	S	C	N
A	−0.7108	+0.1934	−0.4826
B	−0.24	+1.00	−1.76
C	−0.31	+0.09	−0.79

It was shown[40] that increasing the number of substituents at the alkene double bond increases the fraction of the adduct of type **6** containing the isothiocyanate group. For example, a comparison of the results of reactions of $(SCN)_2$ with 2-methylbut-2-ene **12a** and 2,3-dimethylbut-2-ene **12b** in benzene shows that the yield of isothiocyanate **14b** is considerably higher than that of thiocyanate **14a**.



R = H(**a**), Me (**b**).

Under similar conditions, hex-1-ene gives hexane-1,2-diyl dithiocyanate **15** in 42% yield as well as 2-isothiocyanatohexyl thiocyanate **16** and 1-isothiocyanatohexane-2-yl thiocyanate **17** in 27% overall yield.



The observed ratio of the reaction products **15**:(**16**+**17**) is explained[40] by the effect of steric and electronic factors of the substrate and the thiocyanate anion in the step of the formation of reaction products.

It was found[48] that the reaction of *trans*- and *cis*-hex-3-enes with $(SCN)_2$ gives *erythro*- and *threo*-4-isothiocyanatohexane-3-yl thiocyanates **18** and hexane-3,4-diyl dithiocyanates **19**, respectively, as the main reaction products. The ratio of products **18**:**19** depends substantially on the properties of the solvent. In aprotic solvents, this ratio decreases with an increase in the polarity of the solvent, *e.g.*, it is 2.15 in benzene and 0.46 in acetonitrile.



The product ratio of this reaction in low-polar solvents is affected substantially by the addition of iron powder. For example, the ratio of isomers **18** : **19** changes to 0.03 in benzene. The observed ratio of the reaction products was explained[48] in terms of the HSAB concept.[49] In the opinion of Maxwell *et al.*,[48] the ambident thiocyanate anion in non-polar solvents is mostly solvated at the soft sulfur atom (interaction involving charge transfer). This results in charge-controlled attack of the intermediate carbocation by the nitrogen atom. As the dielectric constant of the solvent increases, the direction of the reaction of the SCN^- anion with the intermediate changes from charge-controlled to frontally-controlled with attack by the sulfur atom. A decrease in the fraction of product **18** in acetonitrile can also be explained by an association of the thiocyanate anion with the solvent similar to dipole-dipole interaction.

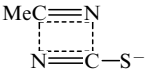


Table 1. Yields of the products of the reaction of styrenes **8a–f** with thiocyanogen in acetic acid.

Compound	R	Product yields (%)		
		9	**10**	**11**
a	4-OMe	78	–	–
b	4-Me	59	~20	21
c	H	36 (44)[a]	~20 (22)[a]	42
d	4-Cl	36	~20	44
e	3-Cl	–	–	85–90
f	3-F	–	–	85–90

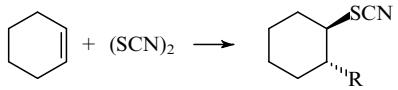
[a] The numbers in parentheses indicate the yields of the products in benzene.

The preferential (84%) formation of dithiocyanate **19** in acetic acid is explained[48] by the coordination of the solvent with the thiocyanate anion with the formation of hydrogen bonds mainly with the nitrogen atom.

Reactions of alkenes with thiocyanogen chloride in acetic acid generally result in products of addition of ClSCN to the alkene double bond and solvato-adducts of the type **7**. For example, the reaction of ethylene with thiocyanogen chloride gives 2-chloroethyl thiocyanate and 2-acetoxyethyl thiocyanate in 64% and 6% yields, respectively.[50] The addition of thiocyanogen chloride to asymmetric aliphatic alkenes occurs both according to and against the Markovnikov rule, whereas solvato-addition always occurs according to the Markovnikov rule. For instance, the reaction of propene with ClSCN in AcOH gives a mixture of adducts: 2-chloropropyl thiocyanate **20** (54%), 1-chloropropane-2-yl thiocyanate **21** (27%), and 2-acetoxypropyl thiocyanate **22** (18%).[51] The ratio of thiocyanates **20**:**21** is the same if the reaction is carried out in chloroform.[52] The reaction of hex-1-ene with ClSCN in AcOH occurs similarly to give 2-chlorohexyl thiocyanate (49%), 1-chlorohexane-2-yl thiocyanate (28%), and 2-acetoxyhexyl thiocyanate (15%).[51] The addition of ClSCN to styrene **8c** obeys the Markovnikov rule to give 2-chloro-2-phenylethyl thiocyanate and 2-acetoxy-2-phenylethyl thiocyanate in 41% and 50% yields, respectively.[51]

2. Stereochemistry of alkene thiocyanation

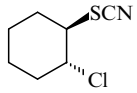
The reaction of $(SCN)_2$ and ClSCN with cyclohexene occurs stereoselectively. The reaction of $(SCN)_2$ with cyclohexene in benzene gives *trans*-isomers of cyclohexane-1,2-diyl dithiocyanate **23** and 2-isothiocyanatocyclohexyl thiocyanate **24**. The reaction in acetic acid gives *trans*-2-acetoxycyclohexyl thiocyanate **25** in addition to the above products **23** and **24**.[40]



23–**25**

Compound	R	Yield (%)	
		in C_6H_6	in AcOH
23	SCN	32	48
24	NCS	16	22
25	OAc	–	24

The reaction of cyclohexene with ClSCN in acetic acid results in *trans*-2-chlorocyclohexyl thiocyanate **26** (77%) and a solvato-adduct **25** (15%).[50]

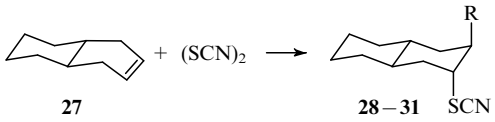


26

Similar results were also obtained in the reaction of $(SCN)_2$ and ClSCN with 4-methylcyclohexene.[40,50] The reaction with $(SCN)_2$ gave *trans*-isomers of 4-methylcyclohexane-1,2-diyl dithiocyanate, 5-methyl-2-isothiocyanatocyclohexyl thiocyanate, and 4-methyl-2-isothiocyanatocyclohexyl thiocyanate.[40] The reaction with thiocyanogen chloride gave a mixture of regioisomeric *trans*-adducts (2-chloro-4-methylcyclohexyl thiocyanate and 2-chloro-5-methylcyclohexyl thiocyanate) and *trans*-solvato-adducts (2-acetoxy-4-methylcyclohexyl thiocyanate and 2-acetoxy-5-methylcyclohexyl thiocyanate).[51]

Reactions with conformationally rigid and conformationally fixed alkenes give products in which the functional groups formed upon the addition of the reagent occupy the *trans*-diaxial positions. For example, the reaction of ClSCN with 5α-2-cholestene in acetic acid results in 2β-chloro- and 2β-acetoxy-3α-thiocyanato-5α-cholestanes in 82% and 11% yields, respectively.[51]

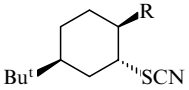
The reaction of thiocyanogen with *trans*-Δ^2-octalin **27** in benzene affords *trans*-decalin-2*a*,3*a*-dithiocyanate **28** (yield 10%) and *trans*-3*a*-isothiocyanatodecalin-2*a*-thiocyanate **29** (yield 5%). If the reaction is carried out in acetic acid, *trans*-3*a*-acetoxydecalin-2*a*-thiocyanate **30** is formed in addition to the adducts **28** and **29**. The yields of decalins **28**–**30** are 40%, 18%, and 21%, respectively.[40] Solvato-adduct **30** and *trans*-3*a*-chlorodecalin-2*a*-thiocyanate **31** were isolated in 25% and 69% yields, respectively, from the reaction mixture of octalin **27** with thiocyanogen chloride.[50]



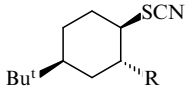
27 **28**–**31**

R = SCN (**28**), NCS (**29**), OAc (**30**), Cl (**31**).

The reaction of 4-*tert*-butylcyclohexene with thiocyanogen in acetic acid gives products **32a**–**c**,[40] while the reaction with thiocyanogen chloride gives compounds **33a**,**b** and **34a**,**b**.[51] The functional groups in compounds **32a**–**c**, **33a**,**b**, and **34a**,**b** have a *trans*-diaxial configuration.



32a,b; **33a,b**



32c; **34a,b**

32a: R = SCN (30%),
32b: R = NCS (6%),
33a: R = Cl (38%),
33b: R = OAc (12%).

32c: R = NCS (6%),
34a: R = Cl (38%),
34b: R = OAc (12%).

The rule of *trans*-addition of thiocyanate-containing reagents also holds for such highly strained alkenes as cyclopropenes.[52,53] The reactions of 3,3-dimethylcyclopropene with thiocyanogen chloride and thiocyanogen in $CHCl_3$ and AcOH afford adducts with *trans*-configuration, namely, *trans*-2-chloro-3,3-dimethylcyclopropyl thiocyanate (80%) and *trans*-3,3-dimethylcyclopropane-1,2-diyl dithiocyanate (20%), respectively.[52]

The reaction of $(SCN)_2$ and ClSCN with stereoisomeric acyclic alkenes is *trans*-stereospecific.[50] Thus, the reaction of thiocyanogen chloride with *cis*-but-2-ene gives 3-chlorobutane-2-yl thiocyanate (81%) and 3-acetoxybutane-2-yl thiocyanate (15%) with *threo*-configurations. The same compounds but with *erythro*-configurations are formed in the reaction with *trans*-but-2-ene. They were isolated in 89% and 8% yields, respectively.

Similar results were obtained in the reaction of thiocyanogen with *cis*- and *trans*-2,5-dimethylhex-3-enes in benzene.[50] In this case, (±)- and *meso*-2,5-dimethylhexane-3,4-diyl dithiocyanates, as well as *threo*- and *erythro*-2,5-dimethyl-4-isothiocyanatohexane-3-yl thiocyanates, respectively, are formed.

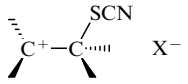
The observed stereochemical features agree with the stepwise reaction scheme and the cyclic structure of the intermediate.[54–56]

The stereoselectivity of addition is violated in reactions with alkenes containing aryl substituents at the double bond. For example, the reactions of *cis*- and *trans*-stilbenes with ClSCN afford a mixture of *threo*- and *erythro*-2-chloro-1,2-diphenylethyl thiocyanates and *threo*- and *erythro*-2-acetoxy-1,2-diphenylethyl thiocyanates. The yield of the adducts was ~50% with predominant formation of the *trans*-isomer. The solvato-adducts are also predominantly of the *trans*-type (the *trans- and cis*-isomer ratio was 9:1; the total yield was ~40%). A mixture of adducts with *threo*- and *erythro*-configuration is formed in dichloromethane, chloroform, and benzene.[57] The reaction of *trans*-1-phenylpropene with $(SCN)_2$ in benzene is also non-stereospecific.[40] However, in this case the total yield of the reaction products does not exceed 20%.

The stereochemistry of the addition of thiocyanate-containing reagents to aryl-substituted alkenes is close to the stereochemistry

observed in reactions of the latter with bromine and its analogues,[58] but differs substantially from the stereochemistry of the addition of sulfenyl halides where high *trans*-stereoselectivity is a typical feature.[54–56]

It was assumed[40,57] that the intermediate **35** with an open structure is formed in the rate-limiting step of the reaction of $(SCN)_2$ and ClSCN with aryl-substituted alkenes.

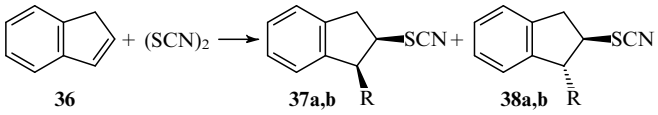


35

X = SCN, Cl.

This assumption agrees well with kinetic data obtained for the reaction of styrenes with thiocyanogen in AcOH.[38]

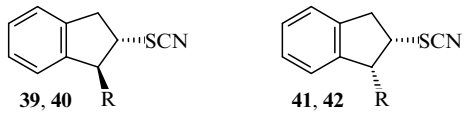
The reactions of thiocyanogen and thiocyanogen chloride with indene and acenaphthylene are not stereoselective, either. Indene **36** reacts with $(SCN)_2$ in benzene to give *cis*- **37a** and *trans*-indane-2,3-diyl dithiocyanates **38a** as well as *cis*- **37b** and *trans*-3-isothiocyanatoindane-2-yl thiocyanates **38b**.[40]



36 **37a,b** **38a,b**

37a: R = SCN, **37b**: R = NCS. **38a**: R = SCN, **38b**: R = NCS.

The reaction with thiocyanogen chloride in acetic acid gives 22% of a mixture of *trans*- **39** and *cis*-3-chloroindane-2-yl thiocyanates **41** (in the 15 : 7 ratio) and 70% of *trans*- **40** and *cis*-3-acetoxyindane-2-yl thiocyanates **42** in which the *trans*-isomer predominates.[51]



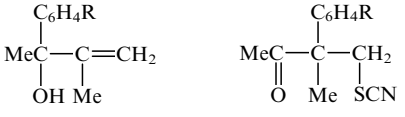
39, **40** **41**, **42**

R = Cl (**39**, **41**), OAc (**40**, **42**).

Acenaphthylene reacts with thiocyanogen chloride in AcOH to give a mixture of *cis*- and *trans*-2-chloroacenaphthenyl thiocyanates in 21 : 79 ratio (total yield 61%) and a mixture of *cis*- and *trans*-2-acetoxyacenaphthenyl thiocyanates in 12 : 88 ratio and in 35% total yield.[57]

3. Molecular rearrangements and proton elimination in reactions of thiocyanogen and thiocyanogen chloride with alkenes

Reactions of thiocyanogen and thiocyanogen chloride with alkenes commonly involve skeletal rearrangements. This was first discovered in a study of a reaction of 2-aryl-3-methylbut-3-en-2-ols **43a–f** with thiocyanogen in a mixture of AcOH with Ac_2O.[59] The main reaction products are thiocyanatoketones **44a–f** formed due to the aryl group migration. The yield of 3-aryl-3-methyl-4-thiocyanatobutan-2-ones **44a–c** is close to quantitative. The yields of ketones **44d–f** were 72%, 60%, and 46%, respectively. The reactions of alkenes **43d–f** give the adducts, namely, 3-aryl-3-hydroxy-2-methylbutane-1,2-diyl dithiocyanates, in addition to thiocyanatoketones **44d–f**.

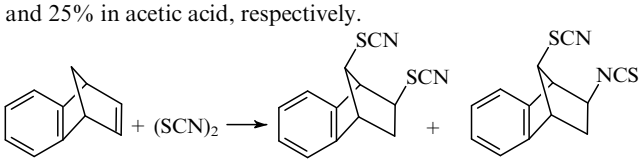


43a–f **44a–f**

R = 4-OMe (**a**), 4-Me (**b**), 3-Me (**c**), H (**d**), 4-Cl (**e**), 3-Cl (**f**).

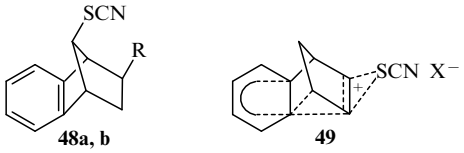
The second-order reaction rate constants (first-order with respect to each reagent) correlate with the Hammett constants of substituents. The reaction constant is negative, $\rho = -2.35$.[59]

The addition of thiocyanogen to benzonorbornadiene **45** in chloroform and acetic acid gives exclusively products of the Wagner–Meerwein rearrangement:[60] 2-*exo*-7-*anti*-dithiocyanato-5,6-benzobicyclo[2.2.1]hept-5-ene **46** and 2-*exo*-isothiocyanato-7-*anti*-thiocyanatobenzobicyclo[2.2.1]hept-5-ene **47**. The total yield of the products is 90%. The relative content of compounds **46** and **47** is 51% and 49% in chloroform and 75% and 25% in acetic acid, respectively.



45 **46** **47**

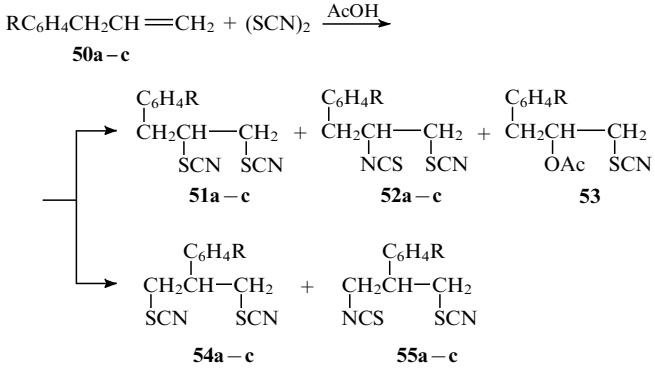
Rearrangement is the only direction of the reaction of benzonorbornadiene with ClSCN. When the reaction was carried out in chloroform, compound **48a** was isolated in 95% yield. In acetic acid, 2-*exo*-chloro- **48a** and 2-*exo*-acetoxy-7-*anti*-thiocyanato-5,6-benzobicyclo[2.2.1]hept-5-ene **48b** are formed in 83 : 17 ratio in 80% overall yield.[60] It is assumed that an ion pair **49** is formed as an intermediate without substantial manifestation of a dative bond.[60]



48a, b **49**

R = Cl (**a**), OAc (**b**) X = SCN, Cl

Rearrangement is also possible in the thiocyanation of allylbenzenes **50**. It was found[42,61] that, in addition to the usual 1,2-addition products **51–53**, these reactions give rearrangement products **54**, **55**.

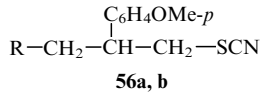


50a–c **51a–c** **52a–c** **53** **54a–c** **55a–c**

R = 4-OMe (**a**), 4-Me (**b**), H (**c**).

The reaction of thiocyanogen with alkene **50a** in a mixture of anhydrous AcOH with acetic anhydride (4 : 1, v/v) gives a product of 1,2-migration of the aryl group, *viz*., 2-(4-methoxyphenyl)propane-1,3-diyl dithiocyanate **54a** in 70% yield.[61] The fraction of rearrangement products decreases abruptly with a decrease in the electron-donating properties of the aryl substituent.[42,61]

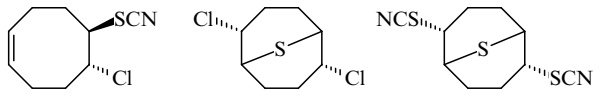
The proportion of rearrangement products formed in the reaction of alkenes **50** with ClSCN is much larger than in the reaction with $(SCN)_2$. For example, the reaction of alkene **50a** with ClSCN in AcOH results only in products of 1,2-shift of the aryl group, *i.e.* 2-(4-methoxyphenyl)-3-chloropropyl thiocyanate (**56a**) and the solvato-adduct **56b**, in the 9 : 1 ratio.[42]



56a, b

R = Cl (**a**), OAc (**b**).

In addition to the main addition product **57**, the reaction of thiocyanogen chloride with (*Z*,*Z*)-cycloocta-1,5-diene in AcOH also gave products of a *trans*-annular reaction, *i.e.* bicycles **58** and **59**.[21] Conversely, the reaction of the same diene with thiocyanogen gives only an adduct, namely, cyclooct-5-ene-1,2-diyl dithiocyanate.[21]



57 **58** **59**

The reactions of $(SCN)_2$ and ClSCN with 1-methylcyclopropene in chloroform and acetic acid have been studied.[52, 62, 63] The reactions occur in several directions to give a mixture of products. In addition to the corresponding adducts and solvato-adducts, addition products with cyclopropane ring opening were isolated.

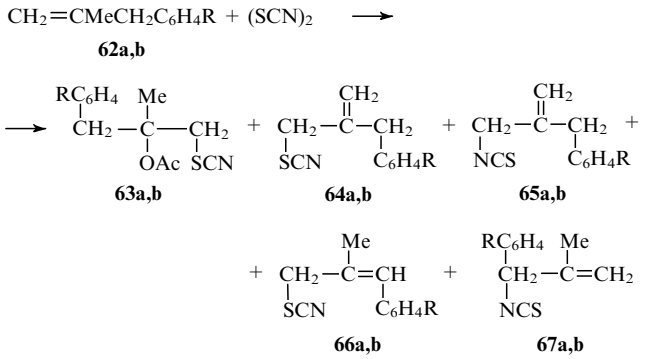
The reaction of $(SCN)_2$ and ClSCN with *gem*-disubstituted alkenes occurs with considerable peculiarities. For example, isobutene reacts with $(SCN)_2$ in acetic acid to give an addition product, methallyl isothiocyanate **60a**, and a solvato-adduct, 2-acetoxy-2-methylpropyl thiocyanate **61**, in a 1 : 4 ratio in 60% – 70% total yield instead of adducts. It is believed[64] that the formation of isothiocyanate **60a** is the result of allyl rearrangement of the thiocyanate **60b** formed initially.



60a,b **61**

R = NCS (**a**), SCN (**b**).

Thiocyanation of 3-aryl-2-methylprop-1-enes **62a**,**b** afforded solvato-adducts (2-acetoxy-3-aryl-2-methylpropyl thiocyanates **63a**,**b**), addition products (**64a**,**b** and **64a**,**b** as a mixture), and products **66a**,**b** and **67a**,**b**. The ratio of the sum of unsaturated products **64a** – **67a** to the acetate **63a** is 1 : 1, and the ratio of compounds **64b** – **67b** to compound **63b** is 1 : 2.[64]



62a,b

63a,b **64a,b** **65a,b**

66a,b **67a,b**

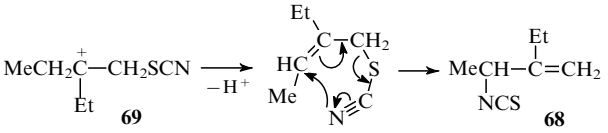
R = H (**a**), 4-Cl (**b**).

Unsaturated compounds are also formed in the reaction of thiocyanogen with 2-methylbut-2-ene in acetic acid.[64]

Similarly, the reaction of isobutene[64] and 2-ethylbut-1-ene[51] with ClSCN in AcOH affords the corresponding unsaturated compounds **60a** and 3-ethylbut-3-en-2-yl isothiocyanate **68** in addition to the adducts and solvato-adducts.

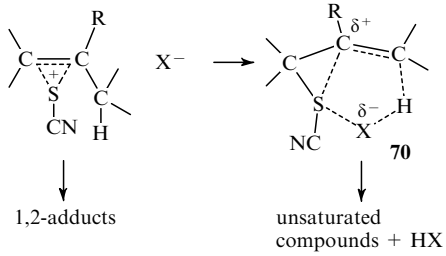
The reactions studied show again that $(SCN)_2$ resembles halogens and interhalogen electrophilic reagents.[58]

It was assumed[51] that unsaturated compounds are formed due to the elimination of a proton from intermediate **69**.



69 **68**

However, an alternative scheme may be suggested for these reactions according to which unsaturated compounds may be formed from a cyclic intermediate through a highly polar intermediate **70**. The stabilising effect of substituents at the β-carbon atom in the carbocationic centre on the intermediate state probably favours such a transformation of the cyclic intermediate.[65]



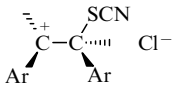
70

1,2-adducts unsaturated compounds + HX

X = SCN, Cl.

Unsaturated compounds are also formed in reactions of ClSCN with phenyl-substituted alkenes. The reaction with 1,1-diphenylethylene afforded a product of the β-proton elimination, *viz*., 2,2-diphenylvinyl thiocyanate, in 10% yield. 1,1-Diphenyl-2-thiocyanatoethanol was also isolated from the reaction mixture. It is believed[51] that this compound is formed as a result of hydrolysis of the adduct formed initially, 2-chloro-2,2-diphenylethyl thiocyanate. The reaction of ClSCN with triphenylethylene gave a β-proton elimination product, 1,2,2-triphenylvinylthiocyanate, in 75% yield.[51]

This reaction is assumed[51] to occur through the formation of the intermediate **71**.



71

Finally, let us consider the data that allow one to deduce the structure of the intermediate formed in the thiocyanation of alkenes. According to some data,[66] the intermediate may have a structure of a π-complex **72** with two electron-deficient S – C bonds without noticeable overlapping of the 3*p*-orbital of the sulfur atom with the π-antibonding orbital of the alkene (dative bond) or of a three-membered cyanosulfonium ion **73** with two ordinary two-electron S – C bonds.



72 **73**

X = SCN, Cl.

Intermediates of the type **73** are assumed to be formed in the sulfenylhalogenation of alkenes.[54, 67, 68] From the formal structural point of view, ClSCN and $(SCN)_2$ can be regarded as sulfenyl chlorides (ClSR) and sulfenyl thiocyanates (NCSSR) in which the hydrocarbon group is replaced by the cyano group. In this case, one should expect a similarity in the chemical behaviour of these two types of electrophilic reagents and formation of intermediates with similar structures.

However, as can be seen from the above data, despite the formal similarity, the thiacyanation of alkenes differs substantially in many respects from the reaction of alkenes with sulfenyl

halides. The formation of rearrangement products and unsaturated compounds, as well as transannular cyclisation and the cyclopropene ring opening, are in better agreement with the assumption that the intermediate in the thiocyanation of alkenes has the structure **72**. In the absence of the dative bond or if it manifests itself insignificantly, the carbon skeleton of π-complex **72** can be largely deficient in electron density. This stimulates the processes described above.

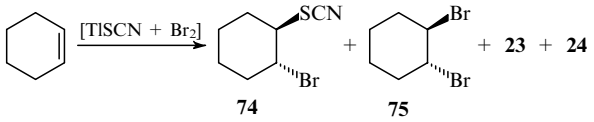
It follows from stereochemical data that in reactions of $(SCN)_2$ and ClSCN with aryl-substituted alkenes, the intermediate **35** with an open structure is more stable than the cyclic one. The sulfenylation of such alkenes occurs *trans*-selectively.[54–56] The difference between thiocyanation and sulfenylhalogenation can be explained by the smaller bond strength in the cyclic intermediate **72** than in the episulfonium ion due to the absence of overlapping of *p*- and π*-orbitals. Therefore, the reaction occurs through a non-cyclic intermediate in the presence of substituents capable of noticeable conjugation with the electron-deficient carbon atom.

Taking into consideration the properties of the media in which these reactions are usually carried out (aprotic and protic solvents with low dielectric constants), one can assume that, irrespective of the exact structure of its cation, the intermediate exists as a tight ion pair, which is possibly in equilibrium with a solvate-separated ion pair.[42, 50, 53, 57, 59, 69] It was assumed[38, 39] that the interaction between the sulfur atom of the cation and the counter-ion exists.

4. Addition of thiocyanogen bromide and thiocyanogen iodide to alkenes

Thiocyanogen bromide has been obtained both in solution[25, 70] and in gas phase.[35] Like ClSCN, it is an unstable compound. The reaction of BrSCN with alkenes has been little studied. The procedure for the preparation of the reagent affects considerably the result of the reaction. In one study,[71] it was prepared by the reaction of bromine with lead thiocyanate in CCl_4. Its subsequent reaction with oct-1-ene resulted in a mixture of 1,2-dibromooctane and 2-bromooctyl thiocyanate. The reaction products were not separated. The conclusion on their structures was done on the basis of GLC and elemental analysis data. It was also assumed that a small amount of 1-bromooctane-2-yl thiocyanate was present in the reaction mixture.

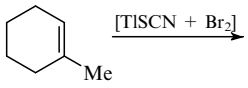
Several procedures were attempted[72] with the aim of obtaining vicinal bromothiocyanates. It was found that the optimum conditions are those where an alkene is treated with an equimolar amounts of bromine and thallium thiocyanate in moist CCl_4 or $CHCl_3$. The reaction of these reagents with cyclohexene gave *trans*-2-bromocyclohexyl thiocyanate **74** as the main product (50%) and small amounts (3%–5%) of *trans*-1,2-dibromocyclohexane **75** and thiocyanates **23** and **24**.

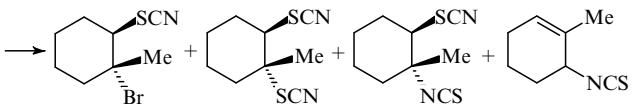


74 **75**

When lead thiocyanate was used, the yield of thiocyanate **74** decreased to 20%.

The reaction of 1-methylcyclohexene with the same reagents gave similar *trans*-addition products **76**–**78** and an unsaturated compound, 2-methylcyclohex-2-enyl isothiocyanate **79**. The structure of *trans*-2-bromo-*cis*-2-methylcyclohexyl thiocyanate **76** indicates that the sulfur atom is the electrophilic centre in the BrSCN molecule.





76 (30%) **77** (21%) **78** (17%) **79** (29%)

The reaction with hex-1-ene is less regioselective. Isomeric products are formed in this case, namely, 2-bromohexyl thiocyanate **80** (44%), 1-bromohexane-2-yl thiocyanate **81** (9%) and compounds **15**–**17** (total yield 18%).

$BuCHR{-}CH_2R'$ **80**: R = Br, R′ = SCN;
80, **81** **81**: R = SCN, R′ = Br.

Styrene **8c** reacts under the conditions specified above to give 2-bromo-2-phenylethyl thiocyanate **82** (44%) and compounds **9c** (18%) and **10c** (12%). The yield of adduct **82** increases to 77% upon the addition of KBr to the reagent.

Unlike in the reactions mentioned above, the reaction of the system bromine–thallium thiocyanate with 2-phenylpropene does not give a vicinal bromothiocyanate. In this case, 2-phenylpropane-2-yl isothiocyanate **83**, 2-phenyl-2-isothiocyanatopropyl thiocyanate **84**, 2-phenylpropane-1,2-diyl dithiocyanate **85**, and 2-phenylpropane-1,2-diyl diisothiocyanate **86** were obtained.



83 (15%) **84** (24%) **85** (24%) **86** (7%)

Under the same conditions, the reactions of *trans*-β-methylstyrene result in *threo*- and *erythro*-1-bromo-1-phenylpropane-2-yl thiocyanates **87** in 11% and 8% yields, respectively, *threo*-1-isothiocyanato-1-phenylpropane-2-yl thiocyanate **88** (11%), and a mixture of *threo*- and *erythro*-1-phenylpropane-1,2-diyl dithiocyanates **89** (total yield 20%).[72]



87 **88** **89**

It is assumed[72] that, depending on the alkene structure, either *S*-cyanosulfonium ion of the type **73** (X = Br) or a cation with an open structure (for aryl-substituted alkenes) are formed as intermediates.

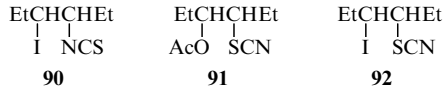
Reactions of alkenes with thiocyanogen iodide are of considerable interest as a method for the synthesis of vicinal iodothio- and iodoisothio-cyanates that can be used efficiently in the synthesis of heterocyclic compounds.[6, 11–14] It is a problem to establish a procedure for the preparation of the reagent that would ensure the selective synthesis of these adducts.

By analogy with thiocyanogen chloride and bromide, ISCN was obtained using the reaction of iodine with thiocyanogen. It should be noted that there is no common viewpoint regarding the position of equilibrium in this system. For example, it was reported[26] that thiocyanogen iodide was formed in a solution in CCl_4; conversely, the formation of a substantial amount of thiocyanogen iodide was considered unlikely in other papers.[35, 73] Nevertheless, although the data presented above are controversial, the use of a solution of iodine and thiocyanogen leads rather smoothly to the formation of iodothio- and iodoisothio-cyanates in many reactions with alkenes.

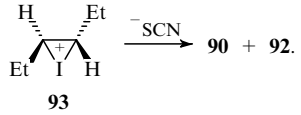
In another method, a system consisting of iodine or iodine-containing electrophiles and salts with the thiocyanate anion were used as the source of ISCN. The advantage of this method is the possibility of varying the reaction conditions over a wide range by changing the properties of the medium and the nature of the salt.

The reaction of *cis*- and *trans*-hex-3-enes with the I_2–$(SCN)_2$ system has been studied.[74] It was found that in benzene, *threo*- and *erythro*-4-iodohexane-3-yl isothiocyanates **90**, respectively, are

formed along with a small amount of the addition product **18**. The same reaction in AcOH results in compounds **18**, **19**, and **91**. It was concluded on this basis [74] that ISCN was not formed in acetic acid. However, a study of the reactivity of the $I_2-(SCN)_2$ system with *trans*-hex-3-ene [6] showed that the *erythro*-adduct **90** and *erythro*-4-iodohexane-3-yl thiocyanate **92** are the main products in benzene, dichloromethane, chloroform, and acetic acid. The ratio of compounds **90** : **92** in AcOH is ~2 : 1 and the total yield is ~60%. In other solvents studied, their ratio changes from 3.5 to 6.0 and the total yield varies from 70% to 80%. Compounds **18**, **19**, and **91** are formed in small amounts.



It was assumed [6] that in all solvents ISCN is the actual electrophile, and, according to the expected polarisation of the reagent, the reaction involves the intermediate **93**.



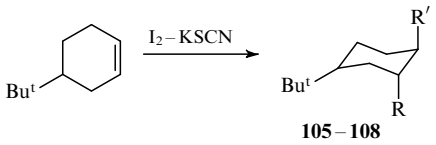
For comparison, the reaction of *trans*-hex-3-ene with the $KSCN-I_2$ system was studied. In chloroform, the ratio of products **92** : **90** is 4 : 1, which differs markedly from that (1 : 6) obtained in the reaction described above. It is believed [6] that the reaction pathways are different.

The $I_2-(SCN)_2$ system reacts with unsymmetrical aliphatic alkenes to give regioisomeric iodothio- and iodoisothiocyanates. The main reaction products with 4-methylpent-1-ene in benzene are 2-iodo-4-methylpentyl thiocyanate **94**, 1-iodo-4-methylpentane-2-yl thiocyanate **95**, 2-iodo-4-methylpentyl isothiocyanate **96**, and 1-iodo-4-methylpentane-2-yl isothiocyanate **97**.[73] The total yield and ratio of the reaction products depend on experimental conditions, in particular on the quality of lead thiocyanate used for the preparation of thiocyanogen solutions. The highest yield of the reaction products (72%) and satisfactory selectivity are observed when the process is carried out in the dark in oxygen-free nitrogen. Iodothiocyanates **94** and **95** were isolated in 17% yield (ratio 3 : 1) and the yield of iodoisothiocyanates **96** and **97** was 51% (ratio 1 : 2).

Similar results were obtained in the reaction with oct-1-ene and 3,3-dimethylbut-1-ene. The reaction with oct-1-ene gives a mixture of 2-iodooctyl thiocyanate **98** and 1-iodooctane-2-yl thiocyanate **99** in 18% total yield (ratio 1.5 : 1) and a mixture of 2-iodooctyl isothiocyanate **100** and 1-iodooctane-2-yl isothiocyanate **101** in 55% total yield (ratio 1 : 2). The reaction with 3,3-dimethylbut-1-ene affords 3,3-dimethyl-2-iodobutyl thiocyanate **102** (10%), 3,3-dimethyl-2-iodobutyl isothiocyanate **103** (40%), and 3,3-dimethyl-2-iodobutane-2-yl isothiocyanate **104** (2%).

In this case, the formation of a iodonium ion of the type **93**, which is attacked by a nucleophile from the less sterically hindered side, is also assumed.[73]

It is noteworthy that with an $I_2-(SCN)_2$ system as the reagent, the proportion of vicinal iodoisothiocyanates in the reaction products exceeds significantly that of iodothiocyanates. It was noted [6] that the fraction of iodothiocyanates formed is substantially larger when the I_2-KSCN system is used. This tendency is also confirmed by the results of the reaction with 4-*tert*-butylcyclohexene in chloroform. Iodothiocyanates **105** and **106** in the 5 : 4 ratio were obtained as the main products (total yield 65%), and the yield of iodoisothiocyanates **107** and **108** was only 12% (ratio 5 : 4).[6]



105: R = SCN, R′ = I; **106**: R = I, R′ = SCN;
107: R = NCS, R′ = I; **108**: R = I, R′ = NCS.

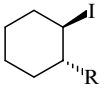
It is assumed that the reaction products mentioned above are formed as a result of diaxial opening of *cis*- and *trans*-iodonium ions. The regioisomeric ratio indicates that the reaction pathway *via* a *cis*-iodonium ion is slightly preferred (5 : 4).[6]

The reaction with 3-*tert*-butylcyclohexene gives *trans*-adduct **109a** and unsaturated compounds **110** and **111**.[6]



109a: R = SCN (36%), **110**: R = I (34%),
109b: R = NCS. **111**: R = NCS (27%).

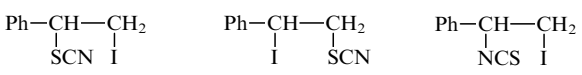
Syntheses of vicinal iodothiocyanates and iodoisothiocyanates were carried out [75, 76] using the ICl–KSCN, I_2–KSCN, and I_2–TlSCN systems in organic solvents and in a water–organic solvent system in the presence of phase transfer catalysts. Methyltrialkyl(C_8-C_{10})ammonium chlorides (Adogen 464) or 18-crown-6 ether were used as catalysts. The structure and yields of the reaction products depend considerably on the reaction conditions. The reaction of cyclohexene with the $KSCN-I_2$ system in a chloroform–sulfolane mixture or in chloroform gives almost exclusively *trans*-2-iodocyclohexyl thiocyanate **112** (96%).



112: R = SCN,
113: R = NCS.

The use of the I_2–TlSCN system in a chloroform–sulfolane mixture at 0–3 °C was found to be optimum for the synthesis of *trans*-2-iodocyclohexyl isothiocyanate. In this case, the yield of isothiocyanate **113** was 60%. In addition, up to 15% of thiocyanate **112** was formed.

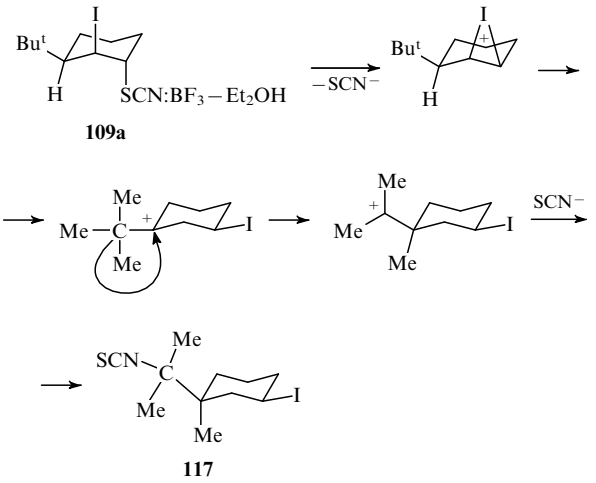
In the reaction with styrene **8c**, the highest yield (72%) of 2-iodo-1-phenylethyl thiocyanate **114** was obtained with the use of the KSCN–ICl system in a chloroform–sulfolane mixture (1 : 9) at 0–3 °C. The selectivity decreases abruptly under different conditions, and 2-iodo-2-phenylethyl thiocyanate **115**, 2-iodo-1-phenylethyl thiocyanate **116**, and products **9c** and **10c** are formed in addition to adduct **114**. Treatment of iodothiocyanate **114** with boron trifluoride etherate in chloroform gives iodoisothiocyanate **116** in 89% yield.



The reaction of β-methylstyrene with the TlSCN–I_2 system in the presence of boron trifluoride etherate occurred most efficiently in $CHCl_3$. In this case, 2-iodo-1-phenylpropyl isothiocyanate (74%) and the product **89** (15%) were isolated.

Thus, performing the reaction in the presence of BF_3 etherate was one of the methods for the selective synthesis of iodoisothiocyanates in the studies cited above.[75, 76] Its addition favours the isomerisation of iodothiocyanates into iodoisothiocyanates. However, this method is not always efficient. For example, such a treatment of thiocyanate **109a** gave compound **117** (26%) instead of the expected isothiocyanate **109b**; the formation of

compound **117** was explained[6] by the migration of the methyl group in the intermediate carbocation.



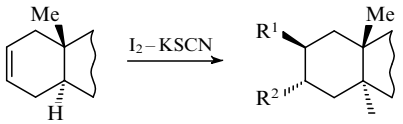
109a **117**

If the reaction is carried out in a chloroform – sulfolane mixture (1 : 9) in the presence of the ICl – KSCN system, the adduct **109b** (yield 51%) is formed along with a small amount (3%) of the product **117**. Performing the reaction under different conditions did not increase the selectivity of the process.

In order to perform selective iodoisothiocyanation of α-methylstyrene, the reaction was carried out either in a chloroform – water mixture (10 : 1) in the presence of the phase transfer catalyst Adogen 464 using the KSCN – I_2 system or in sulfolane with the TlSCN – I_2 system with an addition of boron trifluoride etherate. In these cases, 1-iodo-2-phenylpropane-2-yl isothiocyanate was formed in 71% and 76% yields, respectively.[76]

Iodoisothiocyanation of indene **36** in sulfolane results in *trans*-2-iodoindan-3-yl isothiocyanate **118** and *trans*-2-iodoindan-3-yl thiocyanate **119**. When the reaction mixture was kept for 2 h, compounds **118** and **119** were isolated in 43% and 26% yields, respectively, while after 23 h, adduct **118** was formed preferentially (88%).[76] If the reaction was carried out under different conditions, a more complex mixture of products was formed.

5α-2-Androstene **120** reacts very slowly with the systems considered above. The degree of conversion of this steroid was small when it was treated with I_2 – KSCN in chloroform in the presence of a phase transfer catalyst. After 92 h, a mixture of products was isolated from the reaction mixture: 3α-iodo-2β-isothiocyanato- **121** and 2β-iodo-3α-isothiocyanato-5α-androstanes **122** in the 7 : 1 ratio (total yield 23%); 3α-iodo-2β-thiocyanato- **123** and 2β-iodo-3α-thiocyanato-5α-androstanes **122** in the 5 : 1 ratio (total yield 34%), as well as 3α-iodo-2β-chloro- **125** and 2β-iodo-3α-chloro-5α-androstanes **126** in the 2.4 : 1 ratio (total yield 2%).[76]

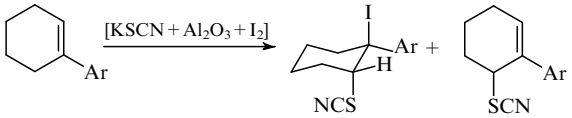


120 **121 – 126**

Product	**121**	**122**	**123**	**124**	**125**	**126**
R^1	NCS	I	SCN	I	Cl	I
R^2	I	NCS	I	SCN	I	Cl

The effect of the metal ion in the system iodine – metal thiocyanate on the reaction with alkenes was studied.[7] In the reaction of this system with cyclohexene, the maximum yield (88%) of the products **112** and **113** and a high selectivity (**113** : **112** = 91 : 9) of the process was observed when $Hg(SCN)_2$ was a component of the system. With TlSCN or AgSCN, the total yield and the selectivity decrease dramatically. The reaction does not occur in the presence of $Ni(SCN)_2$ and $Pb(SCN)_2$. The highest selectivity of the formation of the adduct **112** was achieved with KCSN (**113** : **112** = 3 : 97; total yield 78%). Similar results were obtained for cyclopentene, cycloheptene, and *trans*-hex-3-ene. The reaction with $Hg(SCN)_2$ gives the corresponding iodoisothiocyanates in 65% – 70% yield, and iodothiocyanates are mainly formed (60% – 70%) in the reaction with KSCN. It is assumed[7] that alkenes react with ISCN through a iodonium ion, which reacts with the $I(SCN)_2^-$ complex ion to give iodoisothiocyanates and with $^-$SCN to give iodothiocyanates.

The regioselective synthesis of 2*e*-aryl-2*a*-iodocyclohexyl 1*a*-thiocyanates **127** by the reaction of 1-arylcyclohexenes with a complex system KSCN – Al_2O_3 – I_2 in chloroform was carried out.[77] The yield of thiocyanates **127** was ~40%. In addition to thiocyanates **127**, 2-arylcyclohex-2-enylthiocyanates **128** were obtained in ~60% yield. The formation of the latter is explained[77] by the elimination of a HI molecule from adducts **127**.



127 **128**

Ar = Ph, 4-MeC_6H_4, 3,4-$Me_2C_6H_3$, 4-$Bu^tC_6H_4$, 4-$MeOC_6H_4$.

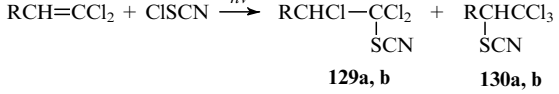
III. Homolytic reactions of thiocyanogen and thiocyanogen halides with alkenes

Homolytic reactions of thiocyanogen and thiocyanogen halides are initiated by ultraviolet irradiation. Under these conditions, thiocyanogen and its halo-derivatives exhibit high reactivity in addition reactions. For example, ClSCN reacts with vinyl chloride, 1,1-dichloroethylene, *cis*- and *trans*-1,2-dichloroethylenes, and other similar compounds under UV irradiation; no reaction occurs without UV irradiation.[78] The yields of reaction products depend on the solvent and the intensity of irradiation. In the reaction of ClSCN with *cis*- and *trans*-1,2-dichloroethylenes, the maximum yield of 1,2,2-trichloroethyl thiocyanate (60%) was obtained in acetic acid in a nitrogen atmosphere; the distance of the reactor from the source of irradiation was 1 cm, and the reaction time was 1 h. Under these conditions, tetrachloroethylene was more inert, and the yield of 1,1,2,2,2-pentachloroethyl thiocyanate was only 11% after 12 h.

Tetraphenylethylene and *trans*-ethylene 1,1-dithiocyanate appeared to be inert under these conditions; the latter was transformed into an equilibrium mixture of *cis* and *trans*-isomers.

The reaction of ClSCN with vinyl bromide affords a mixture of 1-bromo-2-chloro- and 2-bromo-2-chloro-ethyl thiocyanates in 61% and 9% yields, respectively.

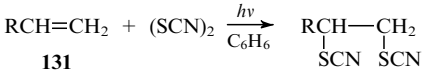
Regioisomeric products are also formed in reactions of ClSCN with 1,1-dichloro- and trichloroethylenes. In this case, 1,1-dichloroethylene gives a mixture of adducts **129a** (55%) and **130a** (4%), and trichloroethylene forms products **129b** and **130b** in 52% and 6% yields, respectively.



129a, b **130a, b**

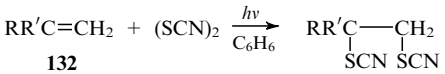
R = H (**a**), Cl (**b**).

A comparison of the results of reactions of thiocyanogen with aliphatic and alicyclic alkenes under homolytic[79] and heterolytic[40] conditions was carried out. The yields of the products are higher in a radical reaction even after shorter reaction times. The reaction with many alkenes is completely selective, *e.g.*, the reactions of alkenes **131** and **132** gives only α,β-dithiocyanates in 70% – 98% yields.[79]



131

R = H, Me, Bu, Bu^t, Me$(CH_2)_7$, Me$(CH_2)_{17}$, Cl, Br, Ph.

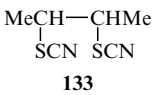


132

R = R′ = Me; R = R′ = Et; R = Ph, R′ = Me.

The reaction of thiocyanogen with 3-methylbut-1-ene is less selective. In addition to 3-methylbutane-1,2-diyl dithiocyanate (63%), unsaturated compounds, *viz*., 2-methylbut-3-ene-2-yl isothiocyanate and 3-methylbut-2-enyl isothiocyanate, are formed.

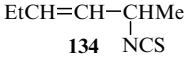
As could be expected, the stereochemistry of the radical reaction differs from that of the heterolytic reaction. *trans*-β-Methylstyrene reacts with $(SCN)_2$ to form adducts **89** with *threo*- and *erythro*-configurations in 14% and 80% yields, respectively. The reaction with *cis*- and *trans*-but-2-enes is not stereoselective. A mixture of (±)- and *meso*-diastereomeric adducts **133** is formed from both isomers. The yields of the adducts are 37% and 57% for the *cis*-alkene and 39% and 60% for the *trans*-alkene.



133

The reaction of thiocyanogen with *cis*- and *trans*-stilbenes is also non-stereoselective. The products of this reaction will be discussed later.

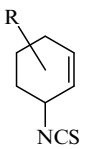
The reaction with *cis*- and *trans*-hex-3-enes occurs in a more complex way. In addition to the adduct **19** (21%), (*E*)-hex-3-en-2-yl isothiocyanate **134** (48%) is formed as a mixture of (±)- and *meso*-diastereoisomers.[79] A somewhat different ratio of the products of this reaction is given by Maxwell *et al*.[48] Compounds **134** and **19** were isolated in 45% and 39% yield, respectively, upon thiocyanation of a *cis*-alkene, and in 60% and 33% yields upon thiocyanation of a *trans*-alkene. In addition, insignificant amounts of adducts with the isothiocyano group were obtained (6.5% and 14.5%, respectively, for *trans*- and *cis*-hex-3-enes).



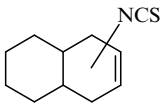
134

The reaction of *cis*- and *trans*-2,5-dimethylhex-3-enes resulted only in products of the substitution of hydrogen at the allylic position, *trans*-2,5-dimethylhex-3-en-2-yl isothiocyanate and 2,5-dimethylhex-4-en-3-yl isothiocyanate, in ~29% total yield.[79]

Unsaturated compounds of the type **135a–c** are formed as the main products in reactions of $(SCN)_2$ with cyclohexene and 4-methyl- and 4-*tert*-butylcyclohexenes (yields 40%–50%).[79] Compounds **135b**,**c** were obtained as a mixture of isomers, and their structure was not fully determined.[79] The reaction with *trans*-Δ^2-octalin **29** occurs similarly to give a mixture of isomeric compounds of the type **136** (the structure was not determined, yield 45%) and the adduct **30** (40%).



135a–c

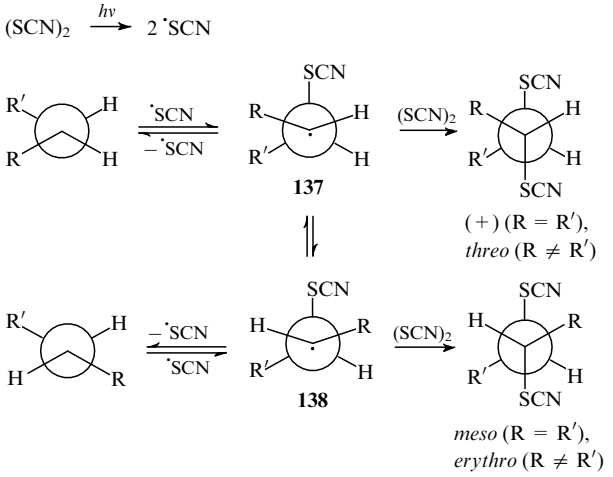


136

R = H (**a**), Me (**b**), Bu^t (**c**).

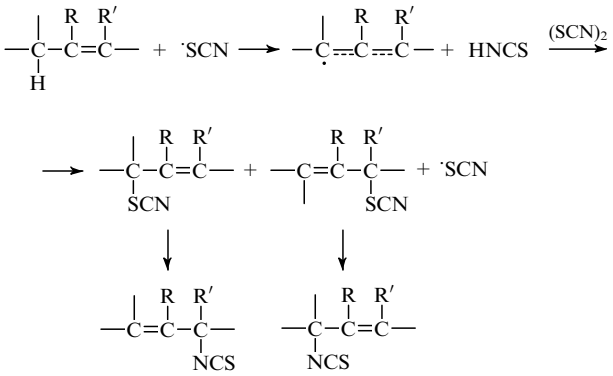
The reactions occur much more slowly in the presence of oxygen and other inhibitors of radical processes. A mechanism presented in Scheme 1 was suggested on the basis of stereochemical data.[79]

Scheme 1

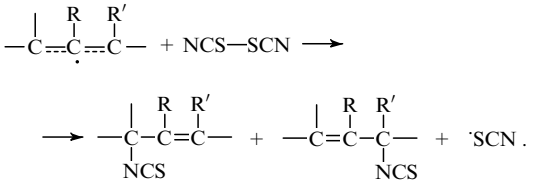


Allylic isothiocyanates are probably formed according to Scheme 2.[79] The primary reaction products include allylic thiocyanates, which isomerise rapidly into more thermodynamically stable isothiocyanates.

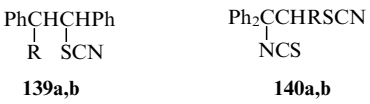
Scheme 2



An alternative scheme was suggested[79] according to which allylic isothiocyanates are formed directly through the reaction of the allylic radical with the nitrogen atom of thiocyanogen, which is more readily accessible sterically.



An increase in the number of methyl groups at the carbon atom of the double bond increases the time required for the reaction. This also leads to a considerable increase in the fraction of adducts of the type **6** in the reaction mixture.[80] This trend also holds for alkenes with phenyl substituents. For example, the reaction of *trans*- and *cis*-1,2-diphenylethylenes gives products with the isothiocyanate groups in 16%–18% yields as a mixture of *erythro*- and *threo*-1,2-diphenyl-2-isothiocyanatoethyl thiocyanates **139a**. However, the main reaction direction is the formation of 1,2-diphenylethane-1,2-diyl dithiocyanates **139b** (a mixture of (±)- and *meso*-forms) in 73% yield. The reaction of $(SCN)_2$ with 1,1-diphenylethylene and triphenylethylene gave 2,2-diphenyl-**140a** and 1,2,2-triphenyl-2-isothiocyanatoethyl thiocyanates **140b**, respectively;[80] α,β-dithiocyanates were not found in the reaction mixture.

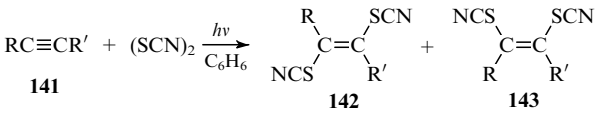


139a,b **140a,b**

R = NCS (**a**), SCN (**b**). R = H (**a**) (54%), Ph (**b**) (11%).

It is seen from the data presented that increasing the number of phenyl groups at the carbon atom of the double bond not only changes the selectivity of the reaction but also decreases the product yields. The increase in the yield of the type **6** adducts with the number of substituents at the double bond is explained [80] by steric effects in reactions of radicals **137** and **138** with thiocyanogen (Scheme 1). With an increase in steric hindrance due to substituents in radicals **137** and **138**, the sterically favourable reaction of these radicals with the nitrogen atom of the reagent becomes more advantageous, leading to the formation of adducts of the type **6**.

Thiocyanogen reacts rather readily with alkynes under homolytic reaction conditions, although this reaction does not occur by the heterolytic mechanism. For example, the reaction of alkynes **141** with an equimolar amount of $(SCN)_2$ gives *trans*- (**142**) and *cis*-1-R-2-R′-ethen-1,2-diyl dithiocyanates **143** in ~90% total yield. *trans*-Isomers are the main reaction products (**142** : **143** ~ 95 : 5). The reaction is over in ~1 h. If the reaction mixture is kept with an excess of thiocyanogen for a longer period the selectivity of the process decreases.[81]

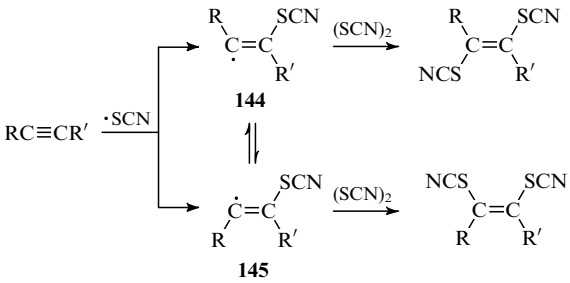


141 **142** **143**

R = H: R′ = H, Bu, Bu^t, Ph;
R = Me, R′ = Ph; R = R′ = Et, Ph.

It is assumed [81] that the reaction occurs according to a chain radical mechanism in which a thiocyanate radical generated photochemically attacks the alkyne to give thiocyanatovinyl radicals **144** and **145**. Probably, the steric and dipole repulsion between the SCN groups of the reactants in the reaction of radical **144** with thiocyanogen is much lower than that in the reaction of $(SCN)_2$ with radical **145**, which results in the preferential formation of *trans*-isomers (Scheme 3).

Scheme 3

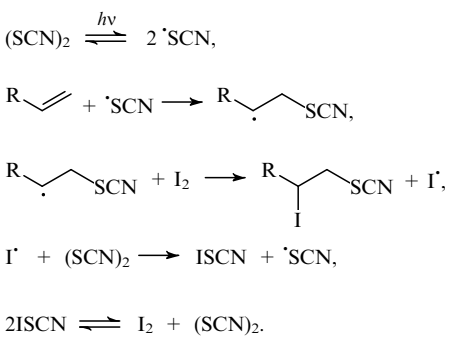


144 **145**

Some specific features of radical reactions of thiocyanogen chloride with alkenes have already been noted above. They are also characteristic of the I_2–$(SCN)_2$ system. In some cases, a homolytic reaction occurs more selectively to give vicinal iodothiocyanates. For example, the yield of the adduct **94** in the reaction with 4-methylpent-1-ene is 80%.[73] A similar reaction with oct-1-ene gives iodothiocyanate **98** (87%) and a small quantity (8%) of products **100** and **101**. 3,3-Dimethylbut-1-ene reacts to give the adduct **102** (76%).[73] It is assumed [73] that the reaction occurs according to Scheme 4.

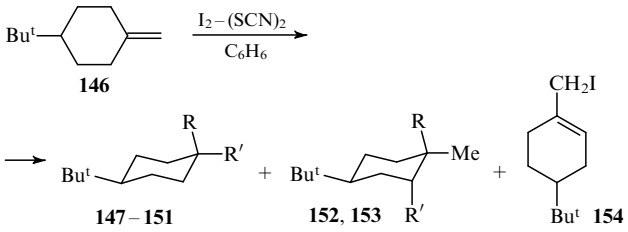
However, this cannot be the common pathway of homolytic reactions. For example, the yield of iodoisothiocyanate **113** in the reaction with cyclohexene is somewhat higher than the yield of iodothiocyanate **112** both in the dark and under irradiation.

Scheme 4



Preferential (60%) formation of iodoisothiocyanates **90** is also observed in the reaction of *trans*- and *cis*-hex-3-enes.[73] The yield of the products of thiocyanation of the alkene **120** in benzene is smaller under illumination (54%) than in the dark (78%), but the fraction of iodothiocyanates **123** and **124** increases simultaneously (37%). The yield of iodoisothiocyanate **121** in the dark is 68%.[73]

The reaction of 4-*tert*-butyl-1-methylenecyclohexane **146** with the I_2–$(SCN)_2$ system gave a complex mixture of products the ratio of which does not change much, no matter whether the reaction is carried out in the dark or under irradiation. However, the total yield is higher in the latter case.[73] A mixture of adducts **147**–**149** was isolated as the main products (48%–63%).



146 **147**–**151** **152**, **153** **154**

Compound	R	R′	Compound	R	R′
147	CH_2NCS	I	**151**	I	CH_2I
148	CH_2I	NCS	**152**	NCS	I
149	NCS	CH_2I	**153**	I	NCS
150	I	CH_2I			

Compounds **147**–**151** are formed upon addition at the exocyclic double bond of alkene **146**, while compounds **152** and **153** are the products of the reaction of 4-*tert*-butyl-1-methylcyclohexene **155**. The latter is formed through the isomerisation of alkene **146**. This conclusion was supported by the fact that compounds **152** and **153** were isolated in 78% yield (ratio 1.8 : 1) from the reaction of the alkene **155** with the same reagent in benzene.

IV. Conclusion

The data considered above make it possible to reveal the basic features of the reactions of thiocyanogen and thiocyanogen halides with unsaturated compounds and to determine their differences from the addition reactions of other electrophilic reagents.

At present, the main attention of researchers is focused on the practical aspects of these reactions, in particular, on the use of the resulting addition products in the synthesis of heterocyclic compounds. Simple and efficient methods for the preparation of iminodithiolane salts,[8] episulfides,[9,11] thiazolines,[6,7,12–14] thiazolidinones,[12] and thiazolidinethiones [10–14] have been elaborated on the basis of products of alkene thiocyanation. Further studies in this field may lead to the creation of a new direction in the synthesis of heterocyclic compounds containing several heteroatoms.

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